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SILICON-CONTAINING TITANIUM DIOXIDE, METHOD FOR PREPARING
THE SAME AND CATALYTIC COMPOSITIONS THEREOF

Field of the Invention

The present invention relates to titanium dioxide. More particularly, the invention relates to a novel modified titanium dioxide, a method for its preparation, a catalyst comprising said novel titanium dioxide and various uses thereof.

Background of the invention

Titanium dioxide, TiO_2 , an important compound having a wide range of utilities, in particular as a catalyst, is generally produced by drying or calcining titanium hydroxide, $\text{Ti}(\text{OH})_4$ (also referred in the art as titanyl hydroxide). Titanium hydroxide itself may be prepared by several methods, using different types of titanium compounds.

Three crystalline forms of titanium dioxide are known in the art: Anatase, Rutile and Brookite. The first crystalline forms, Anatase, is considered favorable for the purpose of catalytic applications (US Patent No. 4,388,288 and US Pat. No. 4,422,958).

The effectiveness of catalytic activity of titanium dioxide, like many other catalysts, is associated with its porous structure. Catalysts having well developed mesoporous and macroporous structure permit not only a high rate of chemical reaction, but also a high rate of diffusion of the reagents into the granules of catalysts, as well as a high

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rate of diffusion of the reaction products out of the granules of catalyst.

Many catalytic processes using titanium dioxide are carried out at elevated temperatures. Under severe conditions, the porous structure of the catalyst may partially collapse, thereby causing a significant reduction of the active surface area, which results in decreasing the catalytic activity of titanium dioxide. A partial transformation of the favorable crystalline form, Anatase, into the less favorable form, Rutile, may be observed during such processes. Quantitatively, the thermal stability of the catalyst may be measured by the change in the specific surface area of a sample subjected to calcination (see, for example, French patent application No. 2,621,577 and European Patent Application No. 0311,515).

Since titanium dioxide is a relatively expensive material, it is most desirable that such a catalyst would possess a prolonged effective period of use. The art has addressed the technical problem of improving the thermal stability of titanium dioxide, in order to allow this catalyst to maintain, as much as possible, its porous structure also under severe conditions. The art has particularly attempted to improve the thermal stability of titanium dioxide by combining it with various additives. Useful agents for this purpose may be selected from the group of aluminum, sodium, potassium, calcium or other chlorides, nitrates and powdery silica.

The art has particularly focused in combining titanium dioxide with silicon dioxide, by means of co-precipitation

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of titanium hydroxide and hydrous silica (silica gel) from an aqueous solution.

Journal of Catalysis 105, p. 511-520 (1987) discloses the co-precipitation of mixed titanium-silicon hydroxide from a solution containing a mixture TiCl_4 and SiCl_4 . The resulting product is described as a support for nickel catalyst.

Precipitation of titanyl sulfate in the presence of a powdery dry silica (SYLOID- -74) was carried out in order to prepare samples containing 20%, 40% and 80% by weight TiO_2 and investigations with these precipitates as catalyst for selective catalytic reduction of nitrogen oxides, were described in Applied Catalysis A, General 139, 1996 . pages 175-187.

Journal of Catalysis, 153, p.165-176 (1995) discloses another method involving the co-precipitation of the mixed titanium-silicon dioxide, using the alkoxide sol-gel method and organic compounds of titanium and silicon as the starting materials, (tetra-isopropoxy-titanium and tetra-methoxysilicon correspondingly). The alkoxide sol-gel method is responsible for the formation of mixed titania-silica aerogels. These porous particles were also tested in the reaction of epoxidation of olefins (Journal of Catalysis 153, 177-189, 1995),

Crystalline titanium silicates having specific adsorption and catalytic properties, prepared by the co-precipitation method, were also described in Advances in Catalysis, Vol. 41, 253-327, 1996.

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Another approach, attempted by the art to modify titanium dioxide via the combination with silica, is described in Applied Catalysis A, General 139, p. 175-187 (1996). According to this publication, titanium hydroxide is precipitated from an aqueous solution in the presence of powdery dry silica (SYLOID -74). The resulting particles exhibit selective catalytic properties for the reduction of nitrogen oxides (NOx).

The review given above emphasizes that there is a growing need to provide a modified titanium dioxide having improved thermal stability.

It is an object of the present invention to provide a method for preparing improved titanium dioxide, which results in the formation of a novel product having enhanced thermal stability and a well developed mesoporous and macroporous structure.

It is an object of the present invention to provide such a method involving the introduction of relatively small amounts of silicon into titanium dioxide structure.

Summary of the invention

The inventors have found an efficient method for producing silicon-containing titanium dioxide with improved thermal stability. The method is based on a reaction of either titanium hydroxide or titanium dioxide with particles of an aqueous silica sol (a colloidal solution of silica). The silicon-containing titanium hydroxide obtained is subjected to a heat treatment, resulting in formation of an improved titanium dioxide possessing enhanced thermal stability. This method is radically different from the methods accepted in

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the art involving co-precipitation of mixed titanium and silicon hydroxides.

The inventors have also surprisingly found that the preferred starting material, for the above mentioned treatment with silica sol, is a precipitate of titanium hydroxide which is obtained from an aqueous solution containing inorganic salts of titanium, following a gradual adjustment of the pH in said solution. This method of precipitation yields titanium dioxide having improved structural features, such as high surface area and a well-developed mesoporous structure. When this precipitate is reacting with silica sol, as explained above, a thermally stable titanium dioxide, having a high surface and developed mesoporous structure, is obtained.

Thus, in one aspect, the present invention is directed to a method for preparing thermally stable, silicon-containing titanium dioxide, said method comprising the reaction of titanium hydroxide or titanium dioxide with a silica sol, under conditions which prevent the coagulation of silica particles in said sol, to obtain silicon-containing titanium hydroxide or silicon-containing titanium dioxide, and in the case of silicon-containing titanium hydroxide, heat treating the same to obtain silicon-containing titanium dioxide.

According to the present invention, titanium hydroxide or titanium dioxide prepared by various methods known in the art may be used as the starting material, generally in the form of a wet cake, an aqueous suspension, a dough or in a dried form. According to a preferred embodiment of the present invention, the starting material is a precipitate of

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titanium hydroxide, obtained by a precipitation method that comprises the following steps:

- a) providing an acidic aqueous solution containing inorganic salts of titanium and, if required, increasing the pH of the solution to a value above 0.02 but below the value at which precipitation of titanium hydroxide occurs, by introducing into said solution a first alkaline agent;
- b) dissolving in said solution a precursor of an alkaline agent, and causing said precursor to generate said second alkaline agent and thereby to precipitate titanium hydroxide in the solution; and
- c) separating and washing said precipitate of titanium hydroxide.

The solution according to step a) comprises inorganic salts of titanium which are preferably sulfate salts. The concentration of titanium in said solution, calculated in terms of TiO_2 , is in the range between 20 to 250 g/l.

Preferably, the first alkaline agent optionally used in step a) is selected from the group consisting of ammonia, hydroxides and/or carbonates of alkali metals or alkaline earth metals.

According to a particularly preferred embodiment of the present invention, a precursor of alkaline agent used in step b) is urea, which, upon heating, is decomposed to generate ammonia. The ammonia produced increases the pH of the solution thereby driving the precipitation of titanium hydroxide.

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The separation of the precipitate according to step c) is accomplished by acceptable liquid/solid separation techniques, for example by filtration. Preferably, following the separation, the precipitate is washed, and used as the starting material in the preparation of a thermally stable, silicon-containing titanium dioxide.

The inventors have found that the novel method of precipitation described above, which constitutes another aspect of the present invention, is important in determining the catalytic properties of the final titanium dioxide. More specifically, this precipitation method imparts the final titanium dioxide a high surface area and a well developed mesoporous structure. These properties are of great importance in the field of catalysts, involving titanium dioxide use. The precipitate of titanium hydroxide, obtained by the method of precipitation described above, may be converted, if desired, into titanium dioxide without a reaction with the silica sol. Due to its structural properties, the resulting silicon-free titanium dioxide is an effective catalyst which can be used in low-temperature catalyzed reactions.

The silica sol used according to the present invention is a colloidal solution containing silica particles, the diameter of said particles being usually in the range of between 1 and 100nm. The concentration of the silica sol is between 1 and 40%, and preferably between 3 and 20% (w/w), calculated as SiO_2 . Preferably, a basic silica sol, stabilized with cations such as Na^+ , K^+ or NH_4^+ is used.

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Preferably the titanium hydroxide or titanium dioxide starting material is treated with an alkaline agent, before its reaction with the silica sol, to adjust the pH of said starting material to a value above 6.0, and preferably between 8 to 10. The reaction between the titanium hydroxide or titanium dioxide and the silica sol is accomplished most effectively under alkaline conditions, wherein the coagulation of the silica particles is prevented and the stability of the sol is maintained. The process is carried out at a temperature between room temperature and the boiling point of the liquid phase of the sol, preferably within the range of 70 to 100°C.

Another aspect of the present invention is directed to a thermally stable titanium dioxide containing not more than 18% silicon, calculated in terms of SiO_2 on dry basis. The said titanium dioxide is a single phase, having essentially the same composition at different points, as determined by the EDAX method. By the term "single phase" is meant a substance consisting of one homogeneous phase, namely, no separate phases of TiO_2 and SiO_2 are observed in said substance.

Another aspect of the present invention is directed to a catalyst, comprising:

- a) at least 3% w/w of a thermally stable titanium dioxide containing not more than 18% silicon calculated as SiO_2 .
- b) A filler, preferably a silica filler; and, optionally
- c) a binder.

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Preferably, the silica filler present in the catalyst is selected from the group of natural silica, namely, diatomaceous earth, optionally treated with an acid to remove impurities therefrom, precipitated silica or silica hydrogels, preferably free of any sodium or potassium contamination.

The binder is optional according to the present invention, and is preferably selected from the group of colloidal solutions of silica or hydrogels of silicic acid.

In the Drawings:

Figure 1 is the X-ray diffraction diagram of a novel titanium dioxide prepared according to the present invention and calcined at 950°C for 1 hour (example 18)

Figure 2 is the X-ray diffraction diagram of a commercially available titanium dioxide UNITi 908 calcined at 950°C for 1 hour.

Figure 3 is the X-ray diffraction diagram of a novel titanium dioxide prepared according to the present invention and calcined at 950°C for 1 hour (example 23).

Detailed description of the invention

The present invention provides a method method for preparing thermally stable, silicon-containing titanium dioxide, said method comprising the reaction of titanium hydroxide or titanium dioxide with a silica sol, under conditions which prevent the coagulation of silica particles in said sol, to obtain silicon-containing titanium hydroxide or silicon-containing titanium dioxide, and in the case of silicon-containing titanium hydroxide, heat treating the same to obtain silicon-containing titanium dioxide.

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As explained above, the preferred starting material according to the present invention is a precipitate of titanium hydroxide, obtained by the following method:

a) providing an acidic aqueous solution containing inorganic salts of titanium and, if required, adjusting the pH of the solution to a value above 0.02 but below the value at which precipitation of titanium hydroxide occurs, by introducing into said solution a first alkaline agent;

b) dissolving in said solution a precursor of an alkaline agent, and causing said precursor to generate said second alkaline agent and thereby to precipitate titanium hydroxide in the solution; and

c) separating and washing said precipitate of titanium hydroxide.

In the following description, the preferred embodiments of said precipitation method will be detailed.

The solution according to step a) comprises inorganic salts of titanium, which are preferably sulfate or chloride salts, most preferably sulfate salts. Examples of particularly suitable solutions are solutions of ammonium titanyl sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$, which is a commercially available compound, or solutions containing titanyl sulfate and sulfuric acid. These solutions of titanyl sulfate and sulfuric acid are either commercially available (UNITi 992TM produced by KEMIRA) or may be prepared by dissolving available titanium hydroxides or titanium dioxides (UNITi 908TM, FINNTiS-230TM) in a concentrated solution of sulfuric acid (70% w/w).

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The concentration of titanium sulfate,, in the solution used according to step a) of the precipitation method, calculated in terms of TiO_2 , is in the range of between 10 and 250 g/l and preferably between 40 and 150 g/l.

The pH of a solution containing titanyl sulfate and sulfuric acid is very low. The pH of the solution is adjusted to a value in the range between 0.02 and the value causing the precipitation of titanium hydroxide by introducing into said solution a first alkaline agent which is selected from the group consisting of ammonia, hydroxides and carbonates of alkali metals or alkaline earth metals. Most preferably, the pH of the solution is adjusted in step b) to a value in the range between 0.8 to 1.7 using ammonia as the alkaline agent. When the starting solution is a solution containing $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$, the pH is already within the required range and usually no adjustment will be required.

A key feature of the method of precipitation, as provided by the present invention, is that the pH adjustment is carried out in a controlled manner. Initially the pH of the solution is increased to a value somewhat below the pH at which precipitation occurs. This may be achieved by using a first alkaline agent. The precipitation is then accomplished by introducing into the solution a precursor of a second alkaline agent. The first and the second alkaline agents may be the same or different. Following homogeneous dispersion of said precursor, the precursor is allowed to generate the second alkaline agent, which actually drives the precipitation of titanium hydroxide. According to a particularly preferred embodiment of the present invention, the second alkaline agent precursor is urea, which, upon heating, is decomposed to generate the second alkaline agent

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itself, i.e. ammonia. The ammonia thus produced increases the pH of the solution, thereby driving the precipitation of titanium hydroxide.

The weight ratio between the quantity of urea, added to the solution according to step b) of the precipitation method, and the quantity of titanium present in the solution (in terms of titanium dioxide) is preferably in the range of between 0.3 to 11.0, more preferably in the range 2-4. Subsequent to the dissolution of the urea, the solution is heated to an elevated temperature, preferably in the range between 90 to 105°C, although other temperatures may also be applicable, whereby ammonia is produced. Most of the titanium hydroxide precipitates quite rapidly, i.e., in several minutes, but preferably, the solution is maintained at said elevated temperature for an additional period of time, to allow a complete precipitation of said titanium hydroxide and concurrently to remove residues of sulfuric acid, which accompany the precipitate. The exact duration of step b) depends on the titanium salt content of the solution, the pH of the solution before the addition of urea, the amount of urea added and the temperature employed. Typically, the duration of step b) is between 1.5-4.0 hours. The value of the pH at the end of this step is above 6.0, usually in the range between 6.2-6.8. The precipitate is separated from the liquid phase, by acceptable methods such as filtration, decantation and centrifugation, and is subsequently washed, preferably by demineralized water.

The precipitate of titanium hydroxide obtained by the precipitation method described above is considered as the preferred starting material for producing silicon-containing titanium dioxide, having enhanced thermal stability,

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according to the present invention. Other titanium hydroxide or titanium dioxide preparations, obtained by a variety of methods known in the art, may be also used as the starting material. For example, titanium hydroxide wet cake precipitated according to the procedure disclosed in EP 722905 A1 (after the washing but without the addition of potassium hydroxide and phosphoric acid to) and titanium hydroxide or titanium dioxide prepared according to US 4,929,586 (before the vanadyl oxalate addition). Additional applicable starting materials are the produced by KEMIRA: UNITi 902TM, FINNTi S-140TM and FINNTi-150TM.

The reaction between the titanium hydroxide or titanium dioxide starting material and the silica sol should be accomplished preferably under conditions ensuring the stability of the sol, namely, conditions preventing the coagulation of the silica particles. For this reason, titanium hydroxide or titanium dioxide starting materials, typically in the form of an aqueous suspension, a wet cake, dough or a dry material, is mixed with an alkaline agent before it is contacted with the silica sol. The alkaline agent is preferably selected from the group of an aqueous solution of ammonia, urea, sodium hydroxide or potassium hydroxide. The pH of the resulting mixture comprising the titanium hydroxide or titanium dioxide starting materials and the alkaline agent should be between 6 to 11, and preferably between 8 to 10. Subsequently, the silica sol is introduced into said mixture, maintaining its stability under said alkaline conditions.

The silica sol used according to the present invention is a colloidal solution containing silica particles. It is known that the inner part of said particles consists essentially

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of dehydroxylated silica, while silicon atoms located on the outer surface of the particles are hydroxylated. Generally, said silica sols contain cations to neutralize the negative charge of the silica particles. The preferred cations are sodium, potassium and ammonium, the latter being most preferred. Methods of preparation of silica sol, for example, those employing a cation exchange method, are well known in the art.

The concentration of the silica sol used according to the present invention is between 1 and 40%, and preferably between 3 and 20% (w/w), calculated as SiO_2 . The quantity of the silica sol contacting with titanium hydroxide or titanium dioxide starting material is such that the weight ratio between silicon and titanium, in terms of their dioxides, is preferably in the range of between 0.01 and 0.3, more preferably in the range of between 0.03 and 0.15. It has been surprisingly found that when said ratio is less than 0.1, substantially all the quantity of silica present in the solution is consumed by the titanium hydroxide or titanium dioxide starting material. The inventors believe that some Ti - O - Si chemical bonds are formed resulting in a reinforcement of the structure of the final titania.

The titanium hydroxide or titanium dioxide is contacted with the silica sol at a temperature in the range between ambient temperature and the boiling point of the liquid phase, preferably in the range 70-100°C. The rate of interaction between the silica sol and the hydroxylated surface of titanium hydroxide or titanium dioxide is temperature dependent, said rate of interaction increasing with the elevation of the temperature.

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Another aspect of the present invention is directed to a thermally stable titanium dioxide containing not more than 18% silicon, calculated in terms of SiO_2 on dry basis. The said titanium dioxide is a single phase, having essentially the same composition at different points, as determined by the EDAX method.

Preferably, the surface area of the silicon-containing titanium oxide is greater than $300 \text{ m}^2/\text{g}$, and its specific pore volume is of at least 0.30 cc/g for pores having a diameter less than 100 nm . The silicon-containing titanium dioxide according to the present invention is thermally stable, as apparent from the following tests:

- i) following calcination at 800°C for 3 hours, it is capable of retaining a surface area above $28 \text{ m}^2/\text{g}$, preferably above $50 \text{ m}^2/\text{g}$, wherein the silicon content, calculated as SiO_2 , is 2%, or above $90 \text{ m}^2/\text{g}$, preferably above $200 \text{ m}^2/\text{g}$, wherein the silicon content, calculated as SiO_2 , is 18%;
- ii) following a hydrothermal treatment at 400°C for 5 hours with a mixture containing 90% by volume water vapor and 10% air, it is capable of retaining a surface area above $120 \text{ m}^2/\text{g}$, preferably above $250 \text{ m}^2/\text{g}$, wherein the silicon content, calculated as SiO_2 , is 18%.

The present invention also provides a catalyst, comprising:

- a) at least 3% of a thermally stable titanium dioxide containing not more than 18% silicon, calculated in terms of SiO_2 on dry basis;
- b) a filler, preferably a silica filler; and, optionally
- c) a binder.

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Preferably, the silica filler present in the catalyst is selected from the group includes both natural silica, namely, diatomaceous earth, optionally treated with an acid to remove impurities therefrom, and precipitated silicas or silica hydrogels, preferably free of sodium or potassium contamination.

In a preferred embodiment of the present invention, the filler is a purified diatomaceous earth, which is obtained after a treatment with an acid, preferably HCl or H₂SO₄, at a temperature in the range of between 20 and 100°C for about 0.5 to 5 hours. Subsequent to a washing stage, diatomaceous earth, substantially free of impurities such as sodium, potassium, calcium, magnesium, aluminum and acid residues, is obtained. Then this diatomaceous earth can be used as a filler according to the present invention.

The binder is optional according to the present invention, and is preferably selected from the group of colloidal solutions of silica or hydrogels of silicic acid.

It is known that the efficiency of a catalyst used in a chemical reaction is dependent on the rate of diffusion of the reaction reagents into the catalyst particulates and the rate of diffusion of the reaction products therefrom. The silica filler is important in determining the macroporous structure of the catalyst. The preferred filler according to the present invention is a diatomaceous earth having a porous structure consisting essentially of macropores, the diameter of which being about 1 micrometer. Precipitated silica with low surface area and without a developed microporous structure and silica hydrogel with similar properties can also be used as fillers.

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The catalyst according to the present invention is preferably prepared as follows. The silicon-containing titanium dioxide (a dried or calcined material) or its silicon-containing titanium hydroxide precursor (in the form of a wet cake, suspension or a partially dried cake) is mixed with the filler material (in the form of a wet cake, partially dried cake, or a completely dried material), and, optionally with a binder. Generally the mixing is facilitated using suitable mechanical means for pastes mixing and malaxating. Optionally, appropriate amounts of water may be added into said mixture in order to obtain a homogeneous dough. The addition of water, however, may not be necessary in cases where the water content of the titanium hydroxide and the filler is sufficient to prepare a paste with the required properties. In some cases the paste has to be dried to a certain extent in the process of dough preparation.

The resulting mixture is shaped into extrudates, beads, tablets, honeycombs or into blocks with any desired shape. The shaped forms obtained above are dried at a temperature in the range of between 50°C-300°C, and are subsequently calcined at a temperature in the range of between 300°C-800°C.

The mixing of the active ingredient with the filler, and optionally, with the binder, yields a mixture which is highly homogeneous, and which may be easily shaped into desirable granules or blocks, having high hardness.

The addition of binder, preferably a sol of silicic acid promotes higher hardness of the granulated material.

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Preferably, the sol is introduced into the mixture containing the active ingredient and the filler in an amount not higher than 20% by weight (calculated in terms of SiO_2). The resulting wet granules may be kept in air for some time or may be dried immediately. The drying process can be conducted at a wide range of temperatures, such as between ambient temperature and 300°C , using different types of dryers. Generally, the wet granules are first dried at a temperature in the range between 100°C - 150°C , to increase their hardness to a degree allowing their loading into a calcination kiln, at a temperature of about 400°C for about 1 to 10 hours. The temperature of calcination may be increased up to 800°C .

The catalyst prepared according to the present invention possesses high thermal and hydrothermal stability and improved mesoporous and macroporous structure. The catalyst is characterized by improved hardness, and because of the excellent properties of active ingredient, relatively small quantities thereof are required to impart the catalyst excellent activity, in comparison to catalysts known in the art.

The novel catalyst of the present invention can be used in various processes, and particularly in processes involving sulfur recovery and in chemical reactions involving sulfur-containing compounds, such as, for example, the reaction of hydrogen sulfide with sulfur dioxide (known as Claus reaction). The following reactions may also be catalyzed using said catalyst: hydrolysis of carbonyl sulfide and carbon disulfide, direct oxidation of hydrogen sulfide with air and tail gases treatment (for example "Sulfreen" process).

The catalyst according to the present may be used in other chemical reactions, in which titanium dioxide is commonly used: the oxidation of carbon monoxide, the reduction of nitrogen oxide with ammonia, the complete oxidation of organic compounds, etc.

All the above description and examples have been provided for the purpose of illustration, and are not intended to limit the invention in any way.

Examples.

Methods of analyses: The modified titanium dioxide and catalysts obtained were analyzed by the following tests for the dry samples as well as for samples calcined at a temperature between 250°C to 900°C:

- determination of the specific surface area, using the so called "1 point method" with Analyzer 4200 (Leeds and Northrup),
- specific surface area and specific adsorption pore volume, as determined with a Coulter Instrument SA 3100,
- macropore structure, as determined by generally accepted mercury intrusion method, and
- the respective chemical analyses, carried out using known tests.

Specific tests of catalytic properties are described in corresponding examples

Preparation A

Preparation of a solution containing dissolved ammonium titanyl sulfate salt

An amount of 2 kg of solid ammonium titanyl sulfate salt containing about 20% of TiO_2 and 27% water, was dissolved in 4 l of demineralized water at room temperature overnight, using a moderate stirring. The non-dissolved portion was separated by filtration. The resulted solution contained 80 g/l titanyl sulfate (calculated as TiO_2) which corresponds to the formula of the respective double salt $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$ and an amount of ammonium sulfate. The pH of this solution was of 0.8.

Preparation B

Preparation of an acidic titanyl sulfate solution

An acidic titanyl sulfate solution, which is compositionally similar to a commercially available acid titanyl sulfate solution, known as "UNITi 992", produced by Kemira Pigments Inc., was prepared as follows:

An amount of 9.8 kg of a commercial titanium dioxide (hydrolysate) UNITi 908, having a loss on ignition of 19.6% by weight (at 1000°C), was dissolved in an amount of 43.8 kg of boiling sulfuric acid having a concentration of 70% by weight. After cooling, an amount of 1 l of this solution was diluted with an equal volume of demineralized water. The resulted solution, having a concentration of 123 g/l TiO_2 , was used in examples 3 to 5. The same solution, but with another concentration of titanium dioxide was used in examples 6 to 18 (see table 2).

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Example 1Preparation of silicon-containing titanium dioxide

Starting material: the solution of ammonium titanyl Sulfate.

Silica sol: basic silica sol containing ammonium cations.

Preparation the precipitate of titanium hydroxide : An amount of 175 g of urea was added to 500 ml of the solution prepared according to preparation A, at room temperature and the resulting solution was heated and maintained at a temperature in the range of between 97-102C for about 3 hours. The precipitated titanium hydroxide was separated from the mother liquor and washed with demineralized water.

Preparation the silicon-containing titanium dioxide: The resulting wet cake of titanium hydroxide was suspended in a basic silica sol, prepared from a commercial sodium silicate solution as known in the art, the pH being increased to about 8.5 by treating with an aqueous solution of ammonia.

In this process an amount of about 41 g of the basic sol was mixed with the titanium hydroxide cake, corresponding to a SiO_2 : TiO_2 weight ratio of about 0.03. The mixture was maintained at about 90°C for 30 minutes under moderate stirring. The residual quantity of silicon in solution was negligible. The wet cake of titanium hydroxide was converted into titanium dioxide, by drying first at 110°C for about 2 hours and further at about 250°C for half hour. The properties of the product obtained are given in Table 1

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below, in comparison to a commercially available titanium dioxide.

Example 2

Preparation of silicon-containing titanium dioxide

Starting material: the solution of ammonium titanyl sulfate.

Silica sol: basic silica sol containing ammonium cations.

The titanium dioxide was prepared as in Example 1, but the amount of the basic silica sol used corresponded to a weight ratio $\text{SiO}_2 : \text{TiO}_2$ to 0.05. The data on the specific surface areas of the prepared sample and the respective thermal stability, compared with a commercially available titanium dioxide, known as UNITi 908, are given in Table 1.

Table 1

Product	Specific surface area of initial titanium dioxide, m^2/g	Weight ratio $\text{SiO}_2 : \text{TiO}_2$	Specific surface area of samples treated with basic silica sol, m^2/g		
			Dried Sample	! After calcination ! for 3 hours, at ! a temperature of 500°C 700°C	
Example 1	392	0.03	436	207	113
Example 2	399	0.05	448	283	144
UNITi 908	328			93	24

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Examples 3 to 5Preparation of silicon-containing titanium dioxide

Starting material: the acidic titanyl sulfate solution.

Silica sol: basic silica sol stabilized with different cations.

Preparation of a precipitate of titanium hydroxide: 1 liter of the acidic titanyl sulfate solution obtained by preparation B was gradually neutralized with 481 grams of an aqueous solution of ammonia, containing about 25% by weight of ammonia. The temperature of the starting solution was 22°C, but, as the heat of the neutralization releases, it may be increased to about 35-55°C. To the above solution, an amount of 780 ml of demineralized water was added and the resulting solution had a pH of 0.90. To the above mentioned solution, an amount of 409 g of urea was added and then heated to 98°C and maintained at this level for about two and half hours (see Table 2). The precipitated titanium hydroxide was separated from the mother liquor and washed with demineralized water. The resulting wet cake was divided into three portions, used in the Examples 3, 4 and 5. Each wet cake sample was diluted with demineralized water, obtaining a suspension which had a concentration of 10% (calculated as TiO_2).

Preparation of silicon-containing titanium dioxide: three basic silica sol was prepared by a method known in the art, using different cations for the sol stabilization; in Example 3: sodium, in Example 4: potassium and in Example 5: ammonium. In each Example, the amount of basic sol used, calculated as % of SiO_2 to TiO_2 was 10% (by weight).

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The three different basic silica sols were mixed separately with the above mentioned three samples of suspension and the resulting mixtures were heated to about 90°C and maintained at this temperature for about 1 hour. In each case, substantially all the quantities of silica were consumed by the titanium hydroxide. The resulted precipitates were separated from the liquid phase by filtration and converted into titanium dioxides by a thermal treatment at four different temperatures: 110°C, 500°C, 700°C and 900°C. The conditions of preparation are given in table 2.

Table 2

Ex. No.	Concentration of titanium hydroxide in the suspension (as % TiO ₂)	Concentration of silica sol (as g/l SiO ₂)	Cationic Form of silica sol	Quantity of silica sol (in terms of % SiO ₂ in TiO ₂)	
				introduced	consumed by Titanium hydroxide
3	10	3.0	Na ⁺	10.0	9.9
4	10	3.0	K ⁺	10.0	9.9
5	10	2.9	NH ₄ ⁺	10.0	9.9

In table 3, values of specific surface area are detailed for titanium dioxide prepared according to examples 3 to 5, before and after the reaction with silica sol.

Table 3

Ex. No.	Specific surface Area of titanium dioxide obtained without the treatment with silica sol (precipitate dried at 110°C)	Specific surface area of titanium dioxide obtained after the treatment with basic silica sol, m ² /g					
		Dried (110°C)	! After calcination ! for 3 hours, at ! a temperature (°C) of	! 500	700	800	900
3	416	442				141	65
4	416	434				139	65
5	416	453	327	277	164		110

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It is apparent that silica sol stabilized with a variety of cations can be used in accordance with the present invention, most preferred being silica sol stabilized with ammonium cation.

Examples 6 to 17

Preparation of silicon-containing titanium dioxide

Starting material: the acidic titanyl sulfate solution.

Silica sol: basic silica sol stabilized with ammonium cations.

In these Examples, an acidic titanyl sulfate solution, according to preparation B, was used as a starting material.

Preparation of a precipitate of titanium hydroxide: The exact conditions for each example (dilution of the starting solution, pH adjustment, amount of urea added and duration of heating of the solution to generate the ammonia) are detailed in table 4.

Table 4

Ex. No.	Concentration of TiO_2 in the starting solution	pH before the addition of urea	Weight ratio Urea: TiO_2	Duration of heating (hours)
6	125	1.10	3.6	2.5
6A	125	1.10	3.6	2.5
7	128	0.80	2.0	2.5
8	128	1.67	2.0	5.5
9	128	1.67	2.0	5.5
10	123	0.8	2.8	2.3
11	70	0.97	2.9	3.5
12	123	0.84	3.6	4.0
13	120	0.97	2.1	3.5
14	126	0.02	10.3	3.0
15	122	0.92	3.6	2.3
16	126	1.20	1.5	2.5
17	91	0.69	2.6	2.2

* In Examples 6 and 6A the solution was maintained at 50°C for 5 hours and 30 minutes, before urea addition;

** In Example 15 the solution was maintained at 53°C for 8 hours after urea addition;

*** In Example 17, the acid titanyl sulfate solution of preparation B was first neutralized with calcium carbonate reaching a pH of 0.09, then the formed calcium sulfate was filtered out. The final neutralization of the solution was carried out with ammonium bicarbonate, reaching a pH of 0.69 as shown in table 4.

Preparation of silicon-containing titanium dioxide: The exact conditions of treating the precipitate of titanium hydroxide (in the form of a suspension or a wet cake) with silica sol, for each example, are indicated in table 5.

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Table 5

Ex. No.	Concentration of titanium hydroxide in the suspension (as % TiO ₂)	Concentration of silica sol (as g/l SiO ₂)	Cationic Form of silica sol	Quantity of silica sol (in terms of % SiO ₂ in TiO ₂)	
				introduced	consumed by Titanium hydroxide
6	10	3.2	NH ₄ ⁺	7.0	6.9
6A	10	3.3	NH ₄ ⁺	15.0	13.8
7	10	3.0	NH ₄ ⁺	2.0	2.0
8	10	3.4	NH ₄ ⁺	3.0	3.0
9	10	3.4	NH ₄ ⁺	7.0	6.0
10	Wet cake	3.2	NH ₄ ⁺	30.0	15.3
11	12	3.3	NH ₄ ⁺	10.0	10.7
12	Wet cake	20.6	NH ₄ ⁺	16.5	13.4
13	15	11.6	NH ₄ ⁺	5.0	5.0

The properties of the titanium dioxides, also in comparison to titanium dioxides known in the art, are given in the following tables.

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Table 6

Ex. No.	Specific surface Area of titanium dioxide obtained without the treatment with silica sol (precipitate dried at 110°C)	Specific surface area of titanium dioxide obtained after the treatment with basic silica sol, m ² /g			
		Dried (110°C)	! After calcination ! for 3 hours, at ! a temperature (°C) of	500	700 800 900
6	424	470	285	170	116
6A	416	478	357	269	203
7	393	393			53 28
8	390	448		111	72 31
9	390	450		170	119 56
10	360		312		228 146
11	403	429			142 81
12	406	430	367	269	
13	400	435	238	141	
14	434				
15	460	490			
16	416				
17	402				
UNITi 908		328	93	24	

Table 7

Hydrothermal stability of the modified titanium dioxides in comparison with commercially available materials.

Example No.	Specific surface area (m ² /g), after steaming* during 5 hours at 400°C
6	173
6A	320
21	132
Commercial TiO ₂ :	
UNITi 908	94
S-150	84

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Note: * the steaming stream contained 90% by volume water vapors, and 10% by volume air.

Table 8Sulfur content of modified titanium dioxides

Sulfur content, (% by weight)

Example No.	Calculated as sulfur	Calculated as (SO ₄ ²⁻)
1	0.04	0.12
5	0.24	0.72
10	0.10	0.30
22	0.07	0.21
Commercial titanium dioxide	0.3-1.0	0.9-3.0

Tabl 9

Specific surface area distribution on pore diameters of
modified titanium dioxides in comparison with known ones

Example	Total specific surface area		Specific surface area formed by pores with a diameter greater than:					
	m ² /g	In % of analogous value for a commercial sample S-140	m ² /g	In % of analogous value for a commercial sample S-140	m ² /g	In % of analogous value for a commercial sample S-140	m ² /g	In % of analogous value for a commercial sample S-140
<u>Example 6</u>								
TiO ₂ before treating with basic silica sol.	424	129	180	253	334	380	352	352
TiO ₂ treated with basic silica sol as described in Example 6	470	143	251	375	352	400	371	371
<u>Example 6 A</u>								
TiO ₂ treated with basic silica sol as described in Example 6A	476	145	319	476	367	417	378	393
<u>Example 15</u>								
TiO ₂ before treating with basic silica sol	490	149	182	272	242	275	259	270
Commercial TiO ₂								
UNITi-908	328	100	48	72	62	70	67	70
Commercial TiO ₂ S-140	329	100	67	100	88	100	96	100

Note: all the data listed in this Table were measured with Coulter Instrument SA 3100.

Table 10

The adsorption pore volume distribution on pore diameters of modified titanium dioxide samples compared with known ones.

Example .	Adsorption pore volume formed by pores with diameter					
	less than 100 nm		greater than 4.1 nm		greater than 3.5 nm	
	cc/g	In % of analogous	cc/g	In % of analogous	cc/g	In % of analogous
	value for commer- cial sample S-140		value for commer- cial sample S-140		value for commer- cial sample S-140	
<u>Example 6</u>						
TiO2 before the treatment with basic silica sol	0.47	147	0.23	110	0.41	178
TiO2 treated with basic silica sol as described in Example 6	0.52	163	0.31	148	0.41	178
<u>Example 6 A</u>						
TiO2 treated with basic silica sol as described in Example 6 A	0.63	180	0.49	233	0.54	235
<u>Example 15</u>						
TiO2 before the treatment with basic silica sol	0.56	160	0.36	171	0.40	174
Commercial TiO2 UNITI- 908	0.32	91	0.20	105	0.22	96
Commercial TiO2 S-140	0.35	100	0.21	100	0.23	100

Note: all the data listed in this Table were measured with Coulter Instrument SA 3100.

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Table 11

Comparison of thermal stability of the modified titanium dioxide prepared according to the present invention and a mixed titania-silica oxide as described in US 4,221,768

Samples prepared according to the present invention and calcined at 500°C for 3 hours			Samples as described in US Patent 4,221,768 (calcined at 500°C for 3 hours)		
Example No.	TiO ₂ content of the sample (% by weight)	Specific surface area (m ² /g)	Example No.	TiO ₂ content of the sample (% by weight)	Specific surface area (m ² /g)
12	86	367	1	84	220
			4	84	280
5	90	327	6	91	230

Table 12

Specific surface areas of calcined titanium dioxide according to the present invention compared with those described in European Patent Applications Nos. 0 576 120 and 0 311 515.

Specific surface area of calcined samples
(m²/g)

temperature of calcination	duration of calcination	The present invention		EP 576120	EP 311515
		Example 6	Example 10	Example 1	Example Q
575	1	229	360		93
575	7	210	350		85
800	3	116	228	65.6	

TABLE 13:

Comparison between structural indicators of calcined samples prepared according to the present invention and those described in the literature.

Prepared according to the present invention					Described in literature				
Example	Quantity of silicon introduced in the titania's structure	Calcining conditions		Specific surface area (m ² /g)	Quantity of silica in titania / silica mixed oxides	Calcining conditions		Specific surface area (m ² /g)	References
	calculated	Temperature	Duration		%	Temperature	Duration		
	as SiO ₂ , %	°C	hours			°C	hours		
5	9.9	700	3	277	20.0	600		85	Applied
6	6.9	700	3	170					Catalysis
8	3.0	700	3	111					A: General
5	9.9	800	3	164					139(1996)
10	15.3	900	3	146					175-187
6	6.9	500	3	285	25.0	500	2	213	Journal
6 A	13.8	500	3	357					of
12	14.0	500	3	367					catalysis
21	7.0	500	3	234					105,511-520
22	15.0	500	3	227					(1987)

It is apparent from the above tables that the novel silicon-containing titanium dioxides are significantly superior, concerning the thermal and hydrothermal stability, over known titania and known titania-silica mixed oxides.

Example 18

Samples of titanium dioxide of Example 6 and of commercially available titanium dioxide (UNITi 908) were calcined at 950°C for one hour. Figures 1 and 2 depict the diffraction

pattern of said calcined samples, respectively. It is apparent from Figure 1 that the thermally stable titanium dioxide of Example 6 maintained the favorable crystalline structure of the Anatase form after the calcination, while the crystalline structure of commercial material (UNITi 908) was partially converted into the catalytically unfavorable Rutile form (Figure 2).

Example 19

The sample prepared in Example 12 was investigated by the EDAX method, to determine the local composition of the titanium dioxide at two different points and the composition of the bulk. The results are detailed in the following table 14:

Table 14

	TiO ₂	SiO ₂	CaO
Point 1	87.5	12.3	0.2
Point 2	87.7	12.3	absent
Bulk	87.8	12.1	0.1

It is apparent from the above table, that, despite very slight variations from one point to another, titanium and silicon are present in each point of the novel titanium dioxide. No separate phases of TiO₂ or SiO₂ exist. The calcium observed is merely a casual impurity in the sample.

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EXAMPLES 20-22.Preparation of silicon-containing titanium dioxides

Starting material: commercially available titanium dioxide
Silica sol: basic silica sol stabilized with ammonium cations.

In these Examples, the process according to the present invention was carried out using commercially available titanium dioxides as the starting material. In Examples 20 and 21, titanium hydrolysates (S-140 and S-150) as produced by KEMIRA PIGMENT OY (Finland) were used. In Example 22, a hydrolysate (UNITi 908) produced by KEMIRA PIGMENT (U.S.A.) was used. The preparation data is summarized in the following table 15:

Table 15Commercial titanium dioxides modified with silica sol.

Example No.	The sample of the TiO ₂ used	Quantity of used TiO ₂ (grams)	Concentration of silica sol as % SiO ₂ in sol	Suspension or wet cake were treated	Quantity of silica sol, as % SiO ₂ calculated on TiO ₂	
					Introduced in the suspension or in the cake	taken up by TiO ₂
20	S-140	200	3.1	suspension	7	
20	S-140	200	3.1	suspension	10	
20	S-140	200	3.1	suspension	14	
21	S-150	200	3.3	suspension	7	
21	S-150	200	3.3	suspension	10	
22	UNITi 908	10	20.6	wet cake	15	13

The properties of the titanium dioxides of the present invention, prepared by using commercially available titanium hydroxides/dioxides as the starting material, are given in table 16:

Table 16

Specific surface areas of commercial titanium dioxides modified with ammonium silica sols.

Ex. No.	Quantity of silica Sol as % SiO ₂ in TiO ₂	Specific surface area of titanium dioxide obtained after the treatment with basic silica sol, m ² /g				
		Dried (110°C)	! After calcination ! for 3 hours, at ! A temperature of ! 500	700	800	900
20	none	329*	16			
20	7		101	58		
20	10		119			
20	14		191	143	94	
21	7	290	234	102	90	
21	10		126			
22	15		227	210	116	80
22	none	328	93	24		

*measured by a Coulter Instrument

The beneficial effects of the method according to the present invention, are evident from the Tables 6, 7, 8.

Example 23

A samples of titanium dioxide of Examples 22 was calcined at 950oC for one hour. Figures 3 depict the X-ray diffraction pattern of said calcined samples. It is apparent from from comparison of Figures 2 and 3 that the thermally stable

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titanium dioxide of Example 22 maintained the favorable crystalline structure of the Anatase form after the calcination, while the crystalline structure of commercial titanium dioxide was partially converted into Rutile form.

Example 24 (comparative)

In this example, an acidic silica sol was introduced directly into a titanyl sulfate solution of preparation B in an amount corresponding to 10% as SiO_2 (calculated on the basis of the TiO_2 content of the solution, present as titanyl sulfate). The titanyl sulfate solution was first diluted to a concentration of 70 g/l of TiO_2 . The pH was adjusted to 0.93 using ammonia, The resulting solution was heated for 2.6 hours (urea: TiO_2 ratio being 3.0), and the precipitation of titanium hydroxide took place in the presence of silica sol.

The precipitate was dried at 110°C, and had a specific surface area of 365 m^2/g . After calcination of 3 hours at 500°C and 700°C, the surface area decreased to 234 and 115 m^2/g , respectively.

Example 25

In this example, acidic and basic silica sols were used and their modifying effects were compared. The criterion of effectiveness was the decrease in the specific surface area of the titanium dioxides as prepared in Examples 13 and 16. In all these experiments corresponding titanium hydroxides were introduced into silica sols having a concentration of 3% calculated as SiO_2 . In one experiment it was an acid sol and in another one, it was a basic sol stabilized with an ammonium cation. As can be noticed from Table 17, both the

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acid and the basic sols produce the stabilizing effect, but the basic sol provides a higher stabilizing effect.

Table 17

Comparison of modificatory effects of acid and basic silica sols.

Example No.	Specific surface area of original TiO ₂ , (m ² /g)	Type of silica sol	Quantity of silica sol, as % SiO ₂ in TiO ₂	Specific surface area (m ² /g), after calcination for 3 hr at a temperature of	
				500°C	700°C
13	400	acidic	8		107
14	400	basic	5	242	145
15	416	acidic	4	155	62
16	416	basic	4	230	123
17	416	without		111	8

Example 26

In this Example the effectiveness of the modified titanium dioxide as an active component of Claus catalyst, is demonstrated.

The modified titanium dioxide as obtained in Example 1, was mixed with powdery silica N60 (produced by PPG) and an acid silica sol. The powdery silica was used as an inert filler and the silica sol was used as a binder component. The composition of this mixture, in weight percentage was as follows:

Modified titanium dioxide	24.9%
Powdery silica	64.6%, and
Silica sol (calculated as SiO ₂)	10.5%

The mixture was granulated into extrudates with a diameter of 3.6 mm, dried at 110°C for two hours and then calcined at 400°C for three hours. The results with this catalyst tested in a bench scale pilot plant, using the known conditions as used in the Claus process were as follows:

$\text{H}_2\text{S} + \text{SO}_2$	100 *
$\text{COS} + \text{H}_2\text{O}$	100
$\text{CS}_2 + \text{H}_2\text{O}$	98.

(*expressed the activity as shown by the conversion related to the equilibrium).

Example 27

This Example shows that the modified titanium dioxide can be used also as a carrier for catalysts which is effective in the oxidation of organic compounds in a gas phase.

Two samples were prepared and tested in a laboratory unit for the catalytic oxidation of propane (3 mol.%) in air at 400°C. In the two cases titanium dioxide was doped with vanadium oxide.

The compositions of the catalysts and the results of the respective tests are given in Table 18. As can be noticed the titanium dioxide as prepared by the present invention, is useful as a catalyst carrier for organic impurities in air oxidation.

Table 18Catalytic oxidation of propane in air at 400°C.

Number of samples from which titanium dioxide was taken	Quantity of vanadia introduced into TiO ₂ (% by weight)	Quantity of doped TiO ₂ in catalyst (% by weight)	Quantity of siliceous filler and binder in catalyst (% by weight)	Extent of oxidation (%)
5	3			100
12	5	38	62	100

Example 28

An experiment was carried out to show that the titanium dioxide prepared according to the present invention can be successfully used as a photocatalyst for the degradation of organic impurities in water by oxidation. The titanium hydroxide precipitated from the acid sulfate solution in the presence of urea and after washing was separated in the form of a wet cake containing 25% by weight TiO₂ before the treatment with basic silica sol (as in Example 7).

The procedure of the testing consists in the use of a suspension of 0.15 - 0.30 grams, calculated as TiO₂ placed in a bottle of 2 l. A quartz tube (internal diameter 1 cm and length 1 m) was used as a sun radiation reactor. Through this reactor and a bottle of water a stream containing 35 to 44 ppm of atrazine was pumped.

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A comparative test with a commercial titanium dioxide (P-25, as produced by Degussa) was used for photodegradation of organic impurities in water. As can be noticed from Table 19, the titanium dioxide prepared according to the present invention can be useful also as a photocatalyst for this reaction.

Table 19Photodegradation of atrazine in aqueous solutions

Sample	<u>Duration of degradation, hours</u>			
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>
<u>Concentration of atrazine in ppm</u>				
Titanium hydroxide				
from Example 7	35	28	23	17
P-25 (Degussa)	44	20		17

Example 29

This example demonstrates the preparation of a catalyst, possessing a high catalytic activity in the Claus process, with the modified titanium dioxide as an active component, powdery precipitated silica as a filler and silica sol as a binder material,

In this example the following starting materials were used:

- Modified titanium dioxide prepared according to Example 1.
- Powdery silica precipitated from a solution of sodium silicate with sulfuric acid.
- An acidic sol of silicic acid.

The modified titanium dioxide and powdery silica were dried at 105°C for 24 hours. After drying, the two materials had losses on ignition values (LOI) as shown in Table 20.

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Acidic sol of silicic acid was prepared from sodium sol of silicic acid using a cation exchange resin C-100 produced by PUROLITE™.

An amount of 0.5 liter of sodium silica sol with a concentration of about 10% by weight, calculated on anhydrous silica dioxide, had been treated with the H-form of the above mentioned cation exchange resin thus obtaining an acid sol of silicic acid having a pH of about 3.0, and a SiO₂ content of 9.8% by weight.

The above materials were mixed in a laboratory mortar in the form of a paste, its composition calculated on dry basis, is given in Table 21.

The paste was passed through a laboratory extruder obtaining extrudates with a diameter of 3.0 mm. The extrudates were dried at 120°C for 3 hours in a laboratory dryer and then calcined at 400°C for 3 hours in a laboratory muffle. The structural properties of the catalyst obtained are given in Table 22. As can be noticed, the quantity of titanium dioxide present in 1 m³ of catalyst bed, is only 140 Kg which is less than the quantity 777-900 kg present in a commercial catalyst (see Table 5). In order to test the catalytic activity of the above prepared extrudates, these were crushed and the fraction between 8 and 12 mesh was separated by sieving and then tested in a bench scale pilot plant using the conditions as for the Claus process. The results of the tests are given in Table 23.

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Example 30.

This example demonstrates that the modified titanium dioxide can be calcined before its incorporation in the mixture with the other components of the catalyst.

The same modified titanium dioxide as in Example 29 was preliminary calcined at 350°C for 5 hours.

The paste mixture was prepared from this titanium dioxide, siliceous filler and a binder in a laboratory mortar (see Table 20); the composition of this paste, calculated on dry basis, is given in Table 20.

The paste had been formed into the same extrudates as in Example 29 in a laboratory extruder and then the extrudates were dried and calcined as in Example 29.

The structural properties of the prepared catalyst are given in Table 22.

The extrudates were crushed and the fraction with sizes of crumbs between 8 and 12 mesh, was tested in a bench scale pilot plant using the conditions as for Claus process. The results are given in Table 23.

Example 31 (comparative)

An experiment was carried out using a commercial titanium dioxide catalyst.

This catalyst was introduced in the same reactor as in Examples 29 and 30. The amount of the titanium dioxide used in this case, was substantially the same as in Example 29. It is apparent from Table 23 that the difference in carbon

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disulfide conversion is equal to 10% which shows that the titanium dioxide present in the novel catalyst is more active than the same amount of titanium dioxide present in a commercial catalyst.

Examples 32- 34

In the preparation of the catalysts samples in a pilot plant, diatomaceous earth "CELITE FC" received from LOMPOS (USA) was used as an inert filler. The chemical composition of this material was as follows:

<u>% by weight</u>	
SiO ₂	85.8
Al ₂ O ₃	3.8
Fe ₂ O ₃	1.2
CaO+MgO	1.1
Na ₂ O+K ₂ O	1.1
P ₂ O ₅	0.2
Loss on ignition	3.6

The physical properties of this material were as follows:

Loose weight (g/liter)	120
Oil absorption (% by weight)	128
Water absorption (% by weight)	280

As natural diatomaceous earth contains some undesirable impurities, such as sodium, potassium, iron, aluminum, it was preliminary purified by an acid treatment. For this purpose hydrochloric or sulfuric acid having a concentration of 15%-20% was used, the temperature during this treatment being between 90o-98o C for about 3 hours. The purified diatomaceous earth was filtered, washed with demineralized

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water and used for the preparation of shapable dough in the form of wet cake or as a dried material. In some cases diatomaceous earth can be used as a filler without a preliminary purification.

In Examples 32, 33 and 34, the purified diatomaceous earth was used .

The titanium dioxide from Example 1 was used as an active component in Examples 32-34 together with a silica hydrogel, prepared by the following procedure, as a binder material: Basic silica sol prepared in its sodium form, having an initial concentration of about 3% (calculated as SiO_2) was evaporated to an extent that its concentration increased to 20-30% by weight. Then this sol was treated with a cation exchanger in order to eliminate the sodium and accordingly to decrease its pH to about 3.0. The resulted acidic sol was treated with an aqueous solution of ammonia until its pH increased up to 6-7 and then it was heated. During the heating coagulation of the sol into hydrogel took place and this hydrogel was used for the mixing with the other components.

The modified titanium dioxide in the form of a wet cake, a purified and dry diatomaceous earth and silica hydrogels were mixed in a double shaft mixer-sigma blade (produced by Sepor). After obtaining a homogeneous mixture, it was slightly dried in order to obtain a proper consistency suitable for extrusion. The extrudates having a diameter of 3.6 mm, were obtained with a piston extruder, dried at 120°C for about two hours and calcined at 450°C for 3 hours.

The losses on ignition are shown in Table 20, the compositions of the catalysts as prepared in a pilot plant

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are given in Table 21 and the properties of the catalysts obtained are given in Table 24.

Examples 35-39

This group of Examples describes the preparation of the novel catalyst in the form of extrudates possessing a high hardness without any binder. In each case the catalyst consists of two components: the modified titanium dioxide and an inert filler, namely purified diatomaceous earth (as obtained in Examples 32-33). Losses on ignition for the components are shown in Table 20 and the compositions of the catalysts are given in Table 21.

In each case the active component was mixed with the inert filler and the resulted mixture was malaxated thus producing a shapable dough using a double shaft mixer, as described in Examples 32 to 34 and a piston extruder as used in a process of granulation. After drying at 120°C the extrudates were calcined in a muffle at a temperature of 450°C for 3 hours.

The following variations exist between the Examples 35 to 39:

In Example 35, diatomaceous earth was introduced as a wet cake after filtration, containing 35% of dry material. The paste was partially dried to 55.2% dry material, and then extruded using a piston extruder.

In other cases, diatomaceous earth was used in the form of a dried material (120°C) having a loss on ignition between 5% to 6% (see Table 20).

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Examples 40 and 41

These Examples demonstrate the possibility of obtaining a hard and thermal stable extrudated catalyst, using stabilized commercial titanium dioxides as described above or its mixture with a precipitated titanium dioxide (Example 41). The properties of catalysts prepared according to Examples 40 and 41 are shown in Tables 20, 21, 24 and 28.

TABLE 20Components used for catalysts preparation:

on Example No.	Modified titanium dioxide (active component) of example	Loss on ignition, weight %	Filler		Binder		Loss
			Name	Loss on ignition, weight %	Name	Loss on ignition, weight %	
29	1	9.1	Powdery silica	7.8	Acidic silica sol	90.2	
30	2	3.0	"	7.8	Acidic silica sol	90.2	
32	1	59.2	Diatoma- ceous earth	5.0	Silica hydro- gel	70.3	
33	1	57.5	"	4.0	Silica hydro- gel	74.5	
34	1	52.3	"	4.0	Silica	79.5	

TABLE 20 (continued)

					hydro- gel
35	10	63.7	"	6.5	absent
36	12	62.5	"	8.0	absent
37	9	70.0	"	5.0	absent
38	6	73.0	"	4.0	absent
39	6A	72.0	"	5.0	absent
40	21 in amount of 37% and 22 in amount of 37%(by weight)	63.0 59.0	"	5.0	absent
41	21 in amount of 55% and 6 in amount of 15%	61.0	"	5.0	absent

Table 21

Compositions of catalysts prepared in laboratory and in a pilot plant on the basis of precipitated modified titanium dioxides (% by weight calculated on dry basis)

EXAMPLES

	LABORATORY					PILOT PLANT						
	29	30	32	33	34	35	36	37	38	39	40	41
Composition												
1. TiO ₂	28.4	28.0	30.0	35.0	35.0	35.0	25.0	40.0	38.0	45.0	74.0	70.0
2. Siliceous component (calculated as SiO ₂)	60.2	61.4	55.0	55.0	55.0	65.0	75.0	60.0	62.0	55.0	26.0	30.0
3. Binder materials:						none	none	none	none	none	none	none
3.1 Acidic silica sol	11.4	10.6	none	none	none							
3.2 Silica hydrogel	none	none	15.0	10.0	10.0							

Table 22.

Structural properties of catalysts prepared in laboratory

Example No.	Tamped bulk density, kg/m ³	Specific surface area, m ² /g	Composition of 1m ³ of a tamped catalyst bed,		
			kg/m ³		
			Silica as a filler	Silica as a binder (from sol)	Titanium dioxide
29	490	134	294	55	140
30	480	137	294	50	134

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Table 23.

Catalytic activity of novel catalysts, prepared in laboratory, in Claus process.

Extent of conversion in reactions

Example No.	H ₂ S + SO ₂		COS + H ₂ O		CS ₂ + H ₂ O	
	Initial Catalyst	Aged Catalyst ²	Initial Catalyst	Aged Catalyst	Initial Catalyst	Aged Catalyst
29	93 ¹	97 ¹	100	100	96	90
30	97 ¹	97 ¹	100	100	97	91
31 compara- rative)	94 ¹	-	-	-	86	-

1 calculated as percentage of conversion at equilibrium state.

2 in all cases aging was carried out in a laboratory with a common hydrothermal treating and sulfating.

TABLE 24.

Properties of catalysts prepared in a pilot plant.

Example No.	Hardness (Crushing strength), kg/extrudate	Specific surface area, m ² /g	Tamped bulk density, kg/m ³	Composition of a 1 m ³ of tamped catalyst bed, kg/m ³		
				TiO ₂	Filler	Binder
32	20	165	635	191	349	95
33	17	175	634	222	222	63
34	12	179	567	198	312	57
35	20	174x	590	207	383	absent
36	12	166x	597	209	388	absent

TABLE 24. (continued)

37	9	144	545	191	354	absent
38	13	-	617	234	383	absent
39	14	220x	640	288	352	absent
40	9	164	800	592 ¹	208	absent
41	11	187	700	490 ²	210	absent

Commercial

Claus

catalyst

based on

titanium

dioxides:

"A"	7	134x	860	777	-	-
"B"	7	124x	1000	900	-	-

Notes to table 24:

1. Mixture of stabilized commercial titanium dioxides (see Table 20).
2. Mixture of stabilized commercial titanium dioxide and precipitated titanium dioxide (see Table 20).
3. The sign x indicates that the values of specific surface area were determined with a Coulter instrument SA 3100. Figures without this sign were measured with an Analyser 4200 (Leeds and Northrup Instruments). In all the Tables the meaning of this sign is as above.

TABLE 25

Adsorption pore volume distribution on pore diameters for the novel catalyst in comparison with the commercial one

Example No.	<u>Adsorption pore volume formed by pores with diameter:</u>					
	less than 100 nm		greater than 4.1 nm		greater than 3.5 nm	
	cc/g	In % of the analogous values for the commercial catalyst "A"	cc/g	In % of the analogous values for the commercial catalyst "A"	cc/g	In % of the analogous values for the commercial catalyst "A"
38	0.33	127	0.31	129	0.32	123
39	0.36	138	0.33	138	0.35	135
Commercial Claus catalyst "A"	0.26	100	0.24	100	0.26	100

Note: all the data listed in this table were measured with the Coulter Instrument SA 3100.

Table 26.

Macropore structure of catalysts prepared in a pilot plant in comparison with known ones.

Example No.	Pore volume formed by macropores with diameter greater than indicated (cc/g)			
	100 nm	200 nm	300 nm	400 nm
Mixture of catalysts from Examples 32, 33 and 34	0.38	0.30	0.20	0.05
Mixture of catalysts from Examples 35, 36 and 37	0.30	0.25	0.20	0.10
Example 38	0.21	0.14	0.05	0.02
Commercial Claus catalysts:				
A:	0.16	0.01	-	-
B:	0.01	less than 0.01	-	-
C:	0.01	less than 0.01	-	-

TABLE 27:

Thermal stability of catalysts prepared in a pilot plant in comparison with known Claus catalysts.

Specific Example No.	surface area of starting catalyst, m ² /g	Specific surface area of the catalyst calcined for 3 hours at indicated temperatures, m ² /g			
		500°C	700°C	800°C	900°C
35	174x			89	58
38	175		121	109	
39	220x	214	146	122	
40	180x	164	118	79	
Commercial Claus catalysts based on TiO ₂ :					
A	134x		28	4	
B	110	103	43	22	8
C	200	112	46	28	17

TABLE 28

Hydrothermal stability of the novel catalyst in comparison with known ones.

Conditions of the hydrothermal treatment:

-temperature: 500°C,

-treating agent: water vapor,

-duration: 5 hours:

Specific surface area (m²/g) of steamed catalyst, calculated:

Example No.	per 1 gram	per 1 cc of tamped layer of a catalyst bed
38	120	74
39	135	86
40	113	90
Commercial catalyst "A"		
based on TiO ₂	66	57
Commercial catalyst "B"		
based on TiO ₂	59	59

TABLE 29.Catalytic activity of catalysts prepared in a pilot plant

Number of test	Catalytic process	Type of installation used for testing	Catalysts from Examples	Extent of conversion in the reactions	
				$\text{H}_2\text{S}+\text{SO}_2$	$\text{COS}/\text{CS}_2+\text{H}_2\text{O}$
1	Claus process	Bench-scale pilot plant	35	89	92
2	Sulfreen process	Big pilot	Mixture of Examples 32,33,34		
	temperature 220°C			44	84
	temperature 250°C			38	90
3	Sulfreen process	Big pilot	Mixture of Examples 35,36,37		
	temperature 220°C			44	84
	temperature 250°C			39	92
4	Sulfreen process	Big pilot	Commercial catalyst "C"		
	temperature 220°C			43	81
	temperature 250°C			37	84

Note: in test 1 the extent of conversion in the reaction $\text{H}_2\text{S}+\text{SO}_2$ is calculated as a percentage of conversion at equilibrium state, in the other tests real values of conversion for the reactions $\text{H}_2\text{S}+\text{SO}_2$ and $\text{COS}/\text{CS}_2+\text{H}_2\text{O}$, both are listed.